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ADP023618

TITLE: The Decomposition of Surrogate Fuel Molecules During Combustion

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TITLE: Army Research Office and Air Force Office of Scientific Research Contractors' Meeting in Chemical Propulsion Held in Arlington, Virginia on June 12-14, 2006

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THE DECOMPOSITION OF SURROGATE FUEL MOLECULES DURING COMBUSTION

F1AT06004G003

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SUMMARY AND OVERVIEW: This project is aimed at developing a chemical kinetic database consisting of the rate constants of fundamental single step reactions that describe the pyrolytic decomposition of surrogate fuels molecules. These reactions represent an integral part of any complete combustion kinetics database. They can be competitive with oxidation processes and hence extend the range of current combustion models to richer mixtures. They lead to the unsaturated fragments that are the inputs to PAH/SOOT models and are therefore necessary for the use of such models for the description of particle formation with realistic fuels.

TECHNICAL DISCUSSION: This project began on February 1, 2006. Work that is being reported here are therefore of a preliminary nature. Our first task was to obtain a series of compounds that can be used as precursors for the formation of the various radicals of interest. A number of compounds have now been obtained and studies have been initiated.

Surrogate fuel mixtures contain compounds that have structural features that are the same as found in real fuels. The type of compounds include linear alkanes, branched alkanes, branched

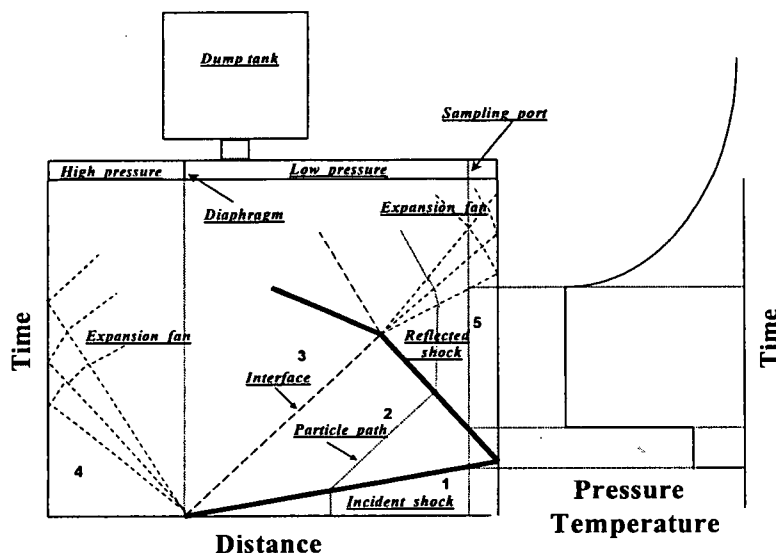


Figure 1: Schematic of single pulse shock tube and associated wave diagrams.

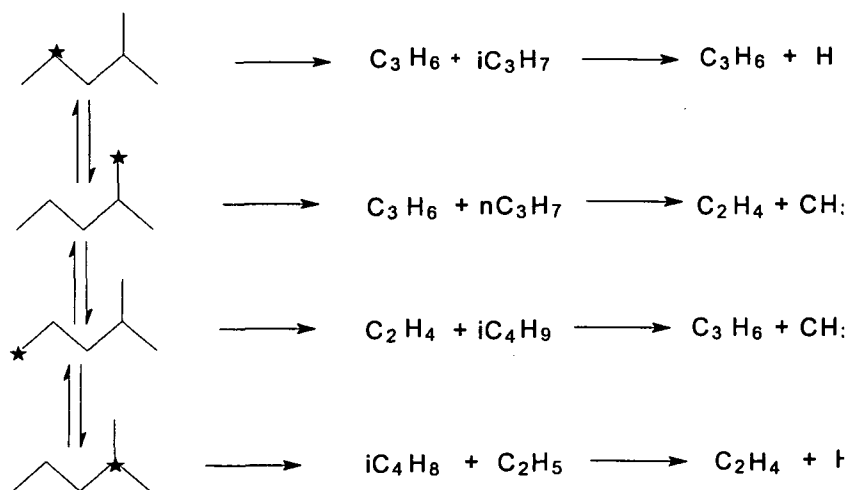


Figure 2: Mechanism for the decomposition of 4-methylpentyl radical. The olefins are those detected from the gas chromatographic analysis.

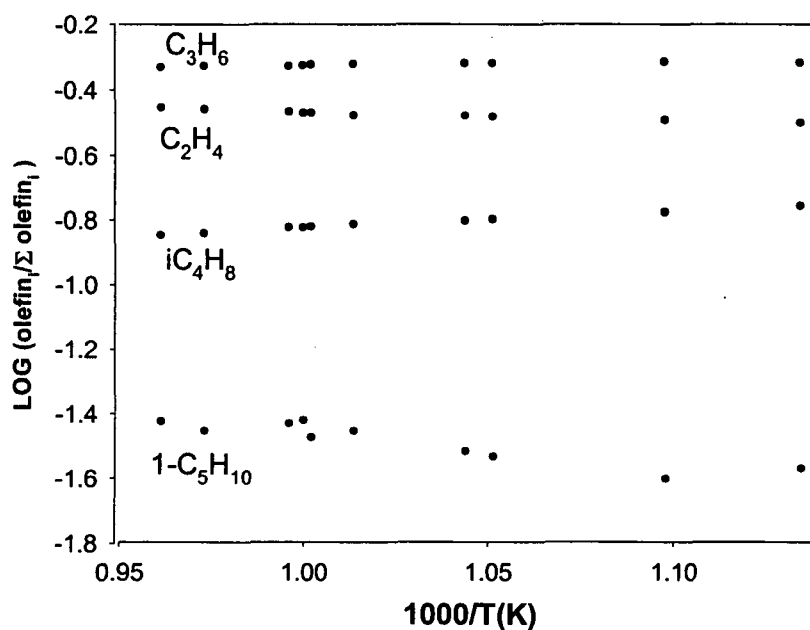


Figure 3: Olefin distribution as a function of temperature from the decomposition of 4-methylpentyl-1 radicals from single pulse shock tube experiments at approximately 3 bar.

cyclanes, and branch aromatics. In a combustion system these compounds are converted into radicals. The radicals can be oxidized or be pyrolyzed. Much of the existing work on combustion models have focused on oxidative degradation. However pyrolytic decomposition is the

shock tube studies is the need for very small samples. We will therefore wait for the analysis of the results before carrying out further studies aimed at discerning the methyl substitution effect for 1-5 hydrogen transfer isomerization in 5-methyl-hexyl radical as derived from the iodide.

We have also carried out preliminary experiments for the decomposition of 1-hexenyl-6 and cyclohexyl radicals. The 1-olefinyl radicals are formed from the 1-olefins that are in turn derived from the decomposition of alkyl radicals. Their decomposition leads to the formation of dienes. These are known to be very important soot precursors. The overall mechanism is very complex and can be seen in Figure 4. There are three isomerization pathways superimposed on beta bond scissions. Previous lower temperature experiments on cyclohexyl radicals have established the relative stability of the cyclic structures (cyclohexyl and cyclopentylmethyl) in comparison to the linear 1-hexenyl-6 radical. In our experiments we see extensive butadiene formation. This is indicative of the more important role of the linear structure at the higher temperatures. In combination with the earlier work, it should now be possible to describe in a quantitative manner the rate constants of the reactions in Figure 4. These results are also of interest in that they shed light on the decomposition of cyclohexyl radicals. This is the result of radical attack on cyclohexane. Cyclohexane type compounds are important components of tar sands. The latter are expected to form increasingly important component of fuel mixtures. Information on their combustion and sooting behavior is expected to be important in the simulation of these new fuels.